

ABSORPTION AND EMISSION SPECTRA
OF NEODYMIUM AND ERBIUM
COMPOUNDS

BY JOHN AUGUSTUS ANDERSON

DISSERTATION

SUBMITTED TO THE BOARD OF UNIVERSITY STUDIES OF THE JOHNS HOP-
KINS UNIVERSITY, IN CONFORMITY WITH THE REQUIREMENTS FOR
THE DEGREE OF DOCTOR OF PHILOSOPHY

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BIOGRAPHICAL NOTE

John Augustus Anderson was born on August 7, 1876, in Tansem, Clay Co., Minnesota. His early education was received in the public schools of his home township, and in those of Moorhead, Minnesota. He entered Valparaiso College in 1898 and received the degree of B.S. in 1901. During the year 1902-03 he taught physics in this college. In the fall of 1903 he entered the graduate department of Johns Hopkins University, taking physics as his principal subject and applied electricity and mathematics as his subordinates. During the years 1903-07 he has attended the lectures given by Professors Ames and Wood in physics, Professor Whitehead in applied electricity, and by Dr. Cohen in mathematics.

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INTRODUCTION

Of the eighteen or twenty elements belonging to the group of rare earths, seven or eight are of special interest to spectroscopists on account of their absorption phenomena. These are neodymium, praseodymium, erbium, holmium, samarium, dysprosium, thulium, and europium. The absorption spectra of solutions of these are remarkable on account of the number and relatively small width of the bands they present, some of which, notably the one near λ 4270, in the aqueous solution of some of the salts of neodymium, may very reasonably be spoken of as lines. These spectra have been the subject of a great number of investigations, a good summary of which may be found in the third volume of Kayser's *Handbuch der Spectroscopie*. In general it may be stated that the solutions of different salts of the same element show very similar absorption spectra, especially when conditions as to concentration and thickness of solution are the same.

The absorption spectra of the crystallized salts of some of these elements have been studied by a number of investigators, the most important work having been done on the crystals of various "didymium" salts by Henri Becquerel.¹ He found that the absorption of

¹ C. R., 104, 1691-1693, 1887; *Ann. Chim. et Phys.* (6), 14, 257-279, 1888

any given crystal depends, to some extent, upon the direction in which the light traverses it, the variation being, however, one of intensity and not of position of the bands. The crystals of different salts, as a rule, show different spectra, in speaking of which he says: "In passing from one spectrum to another, it may be seen, for example, that a given band is displaced, while neighboring bands are not; sometimes a series of bands moves as a whole, while other series are unaffected, . . . finally, some bands, present in one case, may be entirely absent in another." He seems to find in this evidence in favor of the view held by many chemists, that "didymium," or its components, neodymium and praseodymium, are in reality a complicated mixture of several substances, for after comparing the spectra of the crystals with those of their corresponding solutions he says: "In general it may be stated that the spectra of all solutions differ very little from each other, while those of the crystals are quite different. It seems, then, that the matter forming didymium, when in solution is brought into the same condition, and that the presence of different acids in this condition has little or no influence on the absorption."¹ Becquerel also observed that, in case of the dry salts of "didymium," absorption spectra could be observed in white light diffusely reflected from them. The spectra thus observed he found to behave in a way very similar to those observed in crystals.

When the oxides or phosphates of some of these elements, notably erbium and neodymium, are heated to incandescence in a non-luminous flame such as that of a Bunsen burner, the spectrum emitted is not continuous, as in case of most solids and liquids, but consists of some bright bands superposed upon a comparatively faint continuous background. This was first observed in 1866 by Bahr and Bunsen² for the oxide and phosphate of erbium, since which time it has been found that the oxides of neodymium, holmium, and perhaps other elements show similar emission spectra, although they are not as brilliant as that of erbium. Bahr and Bunsen concluded that the emission of the oxide and phosphate of erbium is the same, noting, however, that the bands are more intense with the phosphate. They further concluded that the positions and relative intensities of the

¹ *Ann. Chim. et Phys.* (6), **14**, pp. 257 ff.

² *Liebigs Ann.*, **137**, 1-33, 1866.

bands agree with those of the absorption bands seen in the solutions of erbium salts. Thalén¹ in 1880 came to the same conclusion in regard to the agreement between the bands in the absorption and emission spectra of erbium. Lecoq de Boisbaudran² investigated the emission as well as the absorption of both erbium and neodymium, and found that the emission of erbium phosphate differs considerably from that of its oxide. That this difference was not due to impurities was evident from the fact that both the compounds were made from the same preparation, namely from a solution of erbium nitrate. He also compared them with the absorption spectrum of the chloride, and his drawings show that the agreement is rather poor. About all that can be said is that the two show bands in approximately the same regions of the spectrum, but that they differ considerably both as to intensity and more exact position.

OBJECT OF PRESENT INVESTIGATION

The present investigation was undertaken for the purpose of determining:

1. Whether the emission bands of incandescent erbium oxide really come from the solid itself, or whether they are due to some gaseous layer very close to its surface.

2. How the three kinds of spectra given by some of the elements of the rare earths are related to each other. The three kinds of spectra are:

a) Absorption by solutions of the salts.

b) Absorption by diffuse reflection of white light from the solid compounds.

c) Emission by their incandescent oxides or phosphates.

The elements, erbium and neodymium, were selected partly because the absorption spectra of their solutions show a greater number of bands than those of the other elements, and also because both are known to show very well all three types of spectra mentioned above.

APPARATUS AND METHODS

1. *Salts and solutions.*—The salts and solutions of neodymium were all made from the double nitrate of ammonia and neodymium,

¹ *Comptes Rendus*, 91, 326–328, 376–378, 1880.

² *Spectres Lumineux*, Paris, 1874.

a quantity of which was kindly furnished to Professor H. C. Jones for this and other work by the Welsbach Company of Gloucester, N. J. The anhydrous chloride, sulphate, and nitrate used in making the spectrograms shown in Figs. 8 and 9 were prepared by Professor Renouf, while all the other salts and solutions used were prepared by the author, the procedure being as follows: The double salt was first precipitated by oxalic acid, and the oxalate washed thoroughly with hot water, after which it was dried and heated to a bright red until completely transformed into the bluish-gray oxide Nd_2O_3 , a considerable quantity of which was prepared and kept on hand. From it the sulphate, chloride, nitrate, and acetate were made by simply dissolving it in the corresponding acid.

The erbium preparations used were all made from material which Professor Rowland prepared while he was interested in the separation of the rare earths. It will be remembered that while he was working on the identification of the lines in the solar spectrum he found it difficult or impossible to obtain many of the elements belonging to the group of rare earths in a state of sufficient purity for his purpose. On this account he decided to commence with the original minerals containing these elements, and make an attempt at separating the elements himself, using purely spectroscopic means to guide him in the work. Among the preparations left by him were about a dozen small bottles labelled Erbium "A," Erbium "B," etc., each one containing from two to five grams of oxide. Professor Rowland's notes do not give any definite information about the meaning of the designations on the labels, and hence the contents of each bottle was dissolved in HCl and made up so that all the solutions had, as nearly as possible, the same concentration. On examining the absorption spectra they were all found to be identical as far as the positions and relative intensity of the bands was concerned, but they showed some variation in absolute intensity. The examination of the spectra showed that the solutions were quite free from neodymium and praseodymium, the merest trace of the yellow band of neodymium appearing only when a syrupy solution six or more centimeters deep was used. The bands of holmium, if present at all, were not very strong, indicating that the impurities were chiefly such as give no absorption spectra, and accordingly would, in all probability, not interfere seriously

with the work of the present investigation. The preparations showing the strongest absorption bands, and hence containing the least amount of non-absorbing impurities, were selected and used in the work.

2. *Spectroscopes and photographic plates.*—For visual examination of the spectra, a small direct-vision spectroscope by Steinheil, containing a train of five prisms, was used; while for photographic purposes, a concave grating spectroscope was employed. The grating is a $2\frac{1}{2}$ -inch, of 1 meter focus, ruled with 15,000 lines to the inch.

Since both neodymium and erbium have absorption as well as emission bands in the red, and since the chief group of absorption bands of neodymium lies in the region between λ 5700 and λ 6300, it was very desirable to use a photographic plate sensitive to the yellow, orange, and red. Various makes of films and plates of American manufacture were tried, all of which except Cramer's Trichromatic, were found to give very slight photographic action beyond λ 6100. Cramer's Trichromatic is fairly sensitive to between λ 6300 and λ 6400, but its photographic action is not very even, there being two well-marked minima in the visible spectrum.

The Wratten "Panchromatic," made by Wratten and Wainwright, of Croydon, England, was tried and found so satisfactory that it was used almost exclusively. A brief description of its properties from the standpoint of the worker in spectroscopy may not be out of place here, especially as red sensitive plates, which are at the same time sensitive to the rest of the spectrum, are not very plentiful.

The "Panchromatic" is very sensitive in the red as far as λ 7400, and in the ultra-violet at least as far as λ 2300, and it is almost uniformly sensitive throughout this region. A short exposure will reveal four faint minima at λ 4975, λ 5650, λ 6175, and λ 6675, the one at λ 5650 being much fainter than any of the others. With a full exposure it is very difficult to make out any of these minima, the action being apparently perfectly uniform. When the source is a Nernst filament the action in the red is a little more intense than that in the green or blue, while if the positive crater of the arc is used, the action is greatest in the bluish violet; this indicates a greater absolute sensibility in the bluish violet than in other parts of the spectrum, but the difference is less than in any other plate tried.

The plates are perhaps sensitive farther into the ultra-violet than λ 2300, for the spark used for comparison spectrum in the present work had no strong lines beyond this; so all that can be said is that they are about as sensitive at λ 2300 as the ordinary Eastman or Seed film. The plates must, of course, be developed in absolute darkness, for the light from the ordinary developing lantern fogs them as quickly as the light from a gas-jet fogs an ordinary plate. With this precaution and properly timing the development, there is no difficulty in getting good negatives, perfectly free from fog.

Glass plates could not be bent to the focal curve of the grating, and accordingly they were cut to such lengths (4 to 5 inches) that the definition would still be fairly good over the whole plate.

The region of the spectrum photographed was usually from about λ 3700 to λ 6700, and the dispersion in the first spectrum was such that this could be included on a plate 5 inches long. The plate-holder was movable in a direction parallel to the spectrum lines, and as the plates used were $2\frac{1}{2}$ inches wide, several exposures could be made on one plate, which is indispensable when one is studying changes in the spectrum produced by variations in the conditions under which it is produced.

3. *Methods of observing the emission spectrum.*—In order to observe the emission bands of erbium oxide, all that is necessary is to dip a platinum wire in a fairly concentrated solution of the chloride or nitrate, and then hold it in the flame of a Bunsen burner. The oxide forms a more or less spongy coating over the end of the wire, and when viewed with a direct-vision spectroscope, the characteristic bands may be seen together with a considerable amount of continuous spectrum, part of which may be due to the white-hot platinum wire, but the greater portion in general to the oxide itself. The reason for this is that the spongy coating of oxide takes a very high temperature, and, as was found by Lecoq de Boisbaudran,¹ when the temperature rises the continuous spectrum increases in brilliancy much more rapidly than do the bands. In order, therefore, to see the bands to the best advantage, it is necessary to prevent the oxide from taking too high a temperature. This may be done by making it more compact, by either one of the two following methods:

¹ *Loc. cit.*

a) Bend the end of a platinum wire into the form of a loop, put a small drop of a concentrated solution of the chloride or nitrate on it, and hold it in the flame. After a second or two the substance will be seen to blow out into the form of a tube generally from 2 to 4 mm in diameter and a centimeter or two long, closed at both ends. This tube is extremely thin and hence must be handled with some care to prevent breaking. It should be moistened with the solution and carefully heated again, the operation being repeated perhaps a dozen times, when it will be found that the walls of the tube have become quite thick and compact, or even that the tube has become a fairly compact solid rod, which will stand a considerable amount of rough usage, and which adheres firmly to the platinum wire. If its outer surface is very rough owing to the formation on it of very thin hollow projections, these should be removed; otherwise when the rod is heated, they will take a very high temperature, and hence give rise to the continuous spectrum which it is desired to avoid. Their presence can be readily detected, even when they do not form evident projections, by the fact that when heated they shine with a brilliant green light, quite unlike that of the rest of the rod, which is rather orange due to the bands in the red.

b) This method is based upon the fact that when the oxide of either erbium or neodymium in the form of a fine powder is moistened with a small amount of the chloride solution, it sets after a short time into a rather hard solid mass, a behavior very similar to that of "plaster of Paris" when moistened with water. If this mixture, before it sets, is put into a glass tube having an internal diameter of one or two millimeters, and then just as it is setting is pushed out by means of a close-fitting piston, very smooth, uniform rods of any desired lengths are obtained. A platinum wire may easily be fastened on to one of these rods by wrapping one or two turns of it around the end of the rod, and then covering it over with some of the freshly made mixture. Such a little rod, after having been carefully heated to redness, is generally rather brittle, but may be made quite tough and compact by being repeatedly moistened with the chloride solution and each time slowly heated to redness.

To observe the emission of erbium oxide when heated by cathode rays, vacuum tubes of the form shown in Fig. 1 were used. The

oxide was placed on a piece of platinum foil *A* which was situated at the focus of the concave cathode *D*. The side tube *B* was fitted to the main tube by means of a ground joint *C*, so that it was easy to

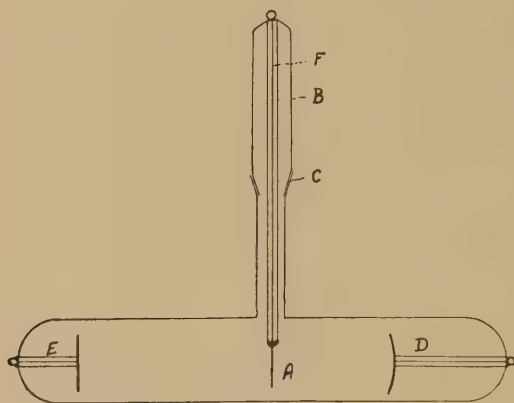


FIG. I.

take out the platinum foil *A* for the purpose of removing the coating of oxide. The wire *F* made it possible to connect the platinum foil to earth or to charge it to any desired potential.

4. *Method of observing the absorption spectra.*—In order to observe the absorption spectrum of the solid

salts it is necessary to focus some strong source of white light, such as the Nernst filament or the positive crater of the arc, on the dry powder, then throw an image of the spot of light on the slit of the spectroscope. For photographing the spectrum of the salts when these were at ordinary room temperatures, they were placed between two small plates of glass, held together with sealing wax; these were placed in such a position that their surfaces were parallel to the jaws of the slit. In order to avoid the light reflected from the glass surfaces, the light from the arc or Nernst filament was made to fall on the plates in such a direction that the angle of incidence was about 45° , in which case the reflected cone of light fell well off to one side. To examine the absorption spectrum when the salts or compounds were kept at temperatures above that of the room, they were spread out into a very thin layer on a piece of platinum foil, which was heated by a Bunsen burner. Various temperatures could be had by placing various thicknesses of sheet asbestos under the foil. This method was found to work satisfactorily up to temperatures of a dull-red heat. To observe or photograph the absorption spectrum at the temperature of the oxide when it is emitting, the arc was focused on the oxide while in the flame of the burner.

For observing the absorption of solutions a number of small cells were made out of a brass tube, the ends being covered by microscope cover glasses. In order to keep the solutions from attacking the brass all that was necessary, was to cover this with a thin coating of shellac.

OBSERVATIONS AND RESULTS

1. *Emission spectrum.*—a) Erbium oxide. The important question to decide in regard to the emission spectrum is whether the bright bands are in reality due to the solid oxide itself, or are to be ascribed to some surface layer of gas, formed by the action of the flame. The simplest and most direct way of settling this would be to heat the oxide without using a flame, for example by placing it on a strip of platinum foil and heating this by passing a current through it. This was tried but no definite results were obtained, because if a thin enough layer is used to allow it to take a temperature approaching that of the platinum strip, the radiation from the layer is so feeble that it is entirely masked by that of the metal, while if a thicker coating is used it does not get hot enough. In one experiment the oxide was highly heated in an electric furnace, but here the light from the porcelain tube of the furnace was overpowering, and besides, since the oxide was practically inside a hollow vessel whose temperature was nearly uniform throughout, nothing but black body radiation was to be expected. It was therefore decided to heat the oxide by cathode rays in a vacuum. This would certainly eliminate the chemical action of the flame, but would still leave the reducing action known to be a property of cathode rays. The method has, however, one great advantage over any flame, and that is that by controlling the vacuum and current-strength, the oxide may be heated to any desired temperature, from that of the room to the most intense white heat, and so is very well suited for the purpose of studying the change in the emission with temperature. As the oxide is heated gradually under the bombardment of cathode rays, the following may be observed:

At temperatures below red heat it gives out a greenish-yellow light, the so-called fluorescent spectrum, already studied and described by Crookes.¹ As the temperature rises the emission

¹ *Proc. R. S.*, 40, 77-79, 1886.

bands in the green soon become visible, and almost simultaneously the bands in the red are seen. The bands in the red always have a considerable amount of continuous spectrum near them, while at low temperatures the bands in the green stand out from a relatively very dark background. With rising temperature the bands in the blue soon become prominent, and the continuous spectrum increases in intensity; simultaneously the bands become more and more hazy, and finally, when the temperature becomes very high, nothing is seen but a perfectly continuous spectrum. At this stage the oxide shines with a light as brilliant as that of a Nernst filament. These appearances were the same whether the platinum strip upon which the oxide was placed was connected to earth, or charged to a high positive potential by being connected to the anode. They were also the same when it was charged to such negative potentials as it was found possible to employ without disturbing the paths of the cathode particles too much. Usually when a negative potential of more than a hundred volts was employed, Wehnelt discharges of slowly moving cathode rays took place which seemed to come from isolated points of the heated oxide rather than from the whole surface. It is possible that the starting-points of these Wehnelt discharges were particles of such impurities as calcium, sodium, or potassium.

When one of these tubes had been used for a few hours, its walls near the strip covered with the oxide became coated with a black deposit. This was at first thought to be platinum, but was shown not to be that by the fact that it could not be dissolved by aqua regia, even when this was boiled in the tube. The only way found to remove the deposit was to scour it out mechanically by means of sand and water, although all the common acids were tried. The deposit was in all probability the metal of the oxides, these being reduced by the action of the cathode rays.

The emission of the oxide when heated in a cyanogen flame was also examined, and found to be identical with that observed when heated in a vacuum, by cathode rays, or when heated in a Bunsen flame. The object of using the cyanogen flame was to eliminate the reducing action of hydrogen.

b) Neodymium oxide. When neodymium oxide is heated in a Bunsen flame it gives a spectrum consisting of two extremely wide,

hazy bands, the intensity-curve of which is shown in Fig. 2. If, however, the oxide be present as an impurity in erbium oxide, it gives a fine series of bands in the yellow and orange, a photograph of which is shown in Fig. 3. It was also introduced as an impurity in calcium oxide, but the bands in this case were very much hazier; that is, the spectrum approached much more nearly that of the pure neodymium oxide.

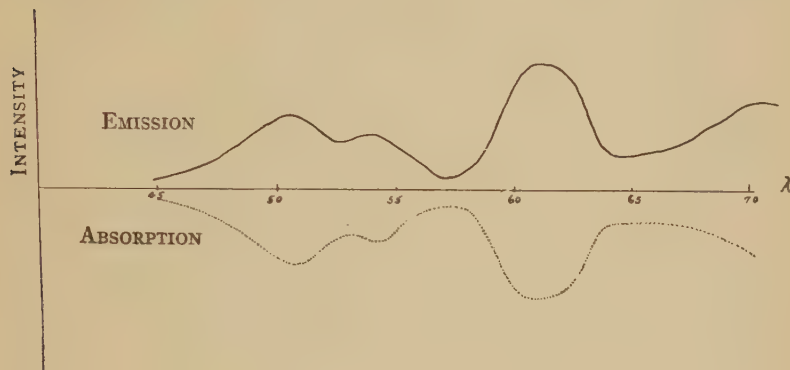


FIG. 2.

2. *Conductivity of erbium and neodymium oxides at high temperatures.*—According to a theory advocated by J. Stark, continuous spectra are due to the free electrons in a substance, and hence we should expect that unless a substance has an appreciable conductivity it should not radiate a continuous spectrum. At temperatures of 1200° C. or below, the continuous spectrum in the light emitted by a bead of erbium oxide is very faint, much more so than is the case with neodymium oxide. It was accordingly of some interest to get at least some relative values of the conductivities of these oxides at high temperatures.

The oxide was made into the form of a Nernst filament by the method already described above. The filaments actually used were about 15 mm long by 2 mm in diameter, and were very compact. This was ascertained by breaking each one after the measurements had been completed; the broken ends showed a very fine-grained structure like that of broken porcelain. They were heated by means of a small platinum furnace, the temperature of which was deter-

mined from resistance measurements made on the heating coil itself.

The conductivity of the filaments was determined by measuring the current through them when an E. M. F. of from 2 to 110 volts was applied; the current being measured by means of a d'Arsonval galvanometer (sensibility = 2.3×10^{-8} amperes).

The following are a few of the values found:

Temperature	SPECIFIC RESISTANCE	
	Neodymium Oxide	Erbium Oxide
1400 C.	1,860 ohms	20,000 ohms
1275 C.	4,000 "	100,000 "
1150 C.	7,500 "	200,000 "

No great accuracy is claimed for these values, the object being rather to find comparative values for the two oxides, than absolute values. They show, however, that at the temperatures given, erbium oxide is a very much poorer conductor than neodymium oxide, and if, as is very probable, the emission of a continuous spectrum is due to the presence of a large number of free electrons, this might suggest an explanation of the fact that neodymium oxide when present as an impurity in erbium oxide emits the bands much better than when by itself. The amount of neodymium oxide needed to give the bands to the best advantage is very small, perhaps less than one per cent., so this would not lower the resistance of the erbium oxide very much.

3. *Absorption by solid compounds.*—a) Erbium oxide. It was stated by Crookes¹ that if a bead of erbium oxide is illuminated with white light and examined with a spectroscope, a group of very fine lines is seen in the green, and he gives a diagram showing the positions of these lines.

Besides this group in the green, there is one in the red, one in the blue, and two in the violet, and also a number of fainter bands in various parts of the spectrum. The intensity of the absorption bands was found to vary considerably with the treatment previously given to the oxide. The three spectrograms reproduced in Plate VIII, Fig. 4, illustrate this. The first (a) is the result of an exposure to the light diffusely reflected from the oxide in the powder form, obtained by heating the oxalate; the oxide used in getting the second (b) was

¹ *Loc. cit.*

PLATE VIII

FIG 3

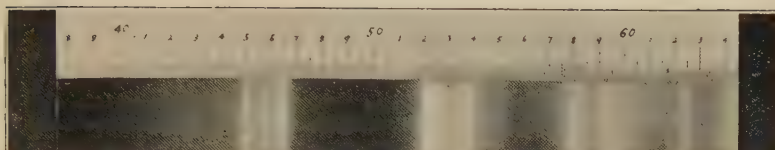
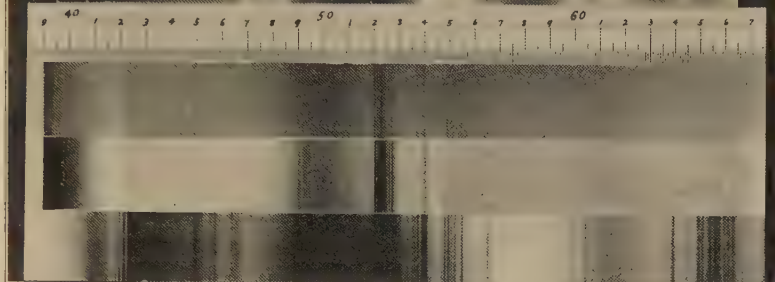


FIG 4

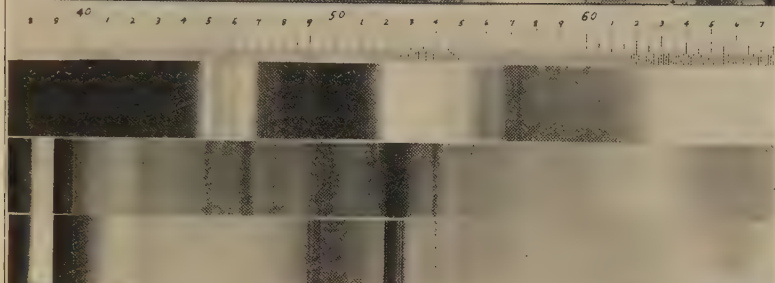


a

b

c

FIG 5.



a

b

c

FIG 6



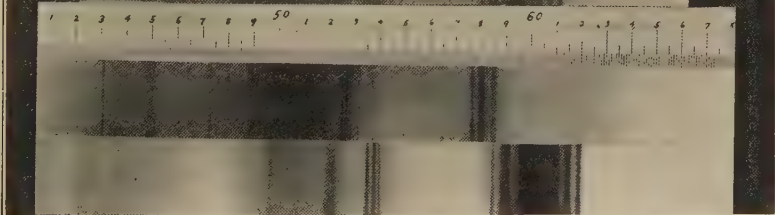
4

3

2

1

FIG 7



in the form of a rod which was made from the chloride solution by the first method described above. It had been heated in the Bunsen flame for at least one hundred hours before this spectrogram was taken. The third spectrum (*c*) was made by employing a rod made according to the second method described above, the rod having been heated in an oxyhydrogen flame for a length of time sufficient to make its surface appear as though it had begun to fuse. The great change in intensity may be explained by the following considerations:

In order that the light diffusely reflected from the solid salts may show absorption bands, it is, of course, necessary that it should have passed through some of the particles of the salt, that is, the light in which the absorption is observed is really transmitted light.

The intensity of the absorption bands will therefore be increased if the length of path traversed by the light in the substance is increased. Now, the fused oxide is probably fairly transparent, for when little rods of it are held in the electric arc for a moment, then withdrawn and allowed to cool, their surface presents a distinctly glassy appearance, which, when held in sunlight and viewed with a spectroscope, shows hundreds of very dark absorption lines or bands. The spectrum is identical with that shown in Fig. 4, *c*, only the bands are very much more intense, and hence a number that are too faint to be seen in the spectrogram, here show quite distinctly. Attempts were made to photograph the spectrum from these fused or glassy surfaces, but it was found so difficult to avoid streaks of continuous spectrum due to reflection from the surface itself, that it was given up.

Returning now to the spectra shown in Fig. 4; when the oxide is in the form of a very fine powder the length of path traversed by the light in the substance itself before it emerges, must be limited to the distance through a very few particles at most, and accordingly, as might be expected, only the strongest absorption bands would be seen. In the second case, where the oxide had been kept at a high temperature for a very long time, incipient fusion had undoubtedly taken place to some extent which would lengthen the path of light in the substance considerably. In the third case the fusion had progressed much farther, although the surface had not assumed the glassy appearance which it gets when the fusion is complete.

It was noticed that the chief groups of absorption bands agree approximately in position with the emission bands when the oxide is heated, and it was natural to assume that the absorption spectrum changes with temperature in such a manner as to become identical with the emission spectrum when high temperatures are reached. This was tried and found to be the case. Fig. 5 shows photographs of the emission spectrum (*a*), absorption spectrum of the oxide while in the flame (*b*), and absorption spectrum of the oxide at ordinary room temperatures (*c*). Visual observations showed that when the temperature is gradually raised the absorption bands became hazy and broaden out, finally running together into the broader bands corresponding to those of the emission spectrum. The individual bands are affected quite differently, as may be seen by noting the changes in the two principal groups in the green. The strongest band in the most refrangible group, as well as the band on its violet side, is shifted toward the red, while the chief band in the less refrangible group is not shifted at all.

The group of bands in the blue is also shifted toward the red somewhat, as is also the group at λ 3780 just beyond the cyanogen bands.

b) Neodymium oxide. The changes produced by change in temperature are also well marked in the case of the absorption of neodymium oxide. These are illustrated by the photograph reproduced in Fig. 6. The first spectrum in the figure shows the absorption of the bluish-gray oxide at a temperature somewhat below 100° C.; the second shows the same for a temperature of about 200°; the third for a temperature of about 400°, and the last one for a temperature of about 600° or a dull-red heat. None of the bands here shows any appreciable shift, but the changes in intensity are in some cases very striking. Consider the fine group of bands lying between λ 6200 and λ 5830. For convenience in speaking of them, they will be referred to by the letters *a*, *b*, *c*, *d*, *e*, *f*, *g*, *h*, and *j*, beginning at the red. Near room temperature, *a*, *b*, and *c* are of nearly equal intensity, *c* being if anything slightly the more intense; *e* and *f* are of about equal intensity, so also *g* and *h*, while *j* is rather more intense than *h*. At 200° C., all the bands have widened somewhat, and the changes in intensity are about as follows: *c* has decreased very much, its intensity being

distinctly less than that of *a* and *b*, which are still equal; *d* has almost disappeared; the intensity of *f* is less than that of *e*, that of *h* very much less than that of *g*; while the intensity of *j* has decreased to less than one-half of its value at the lower temperature. A glance down the spectrum toward the violet shows that the group comprised between λ 4800 and λ 5500 has practically disappeared with a temperature-change of only a little more than 100° C. The bands at λ 4475 and λ 4427 have changed scarcely at all, while that at λ 4382 has had its intensity reduced to about half-value.

At 400°, the bands have widened still more. *a* and *b* are now the most prominent bands in the yellow group, with *b* slightly more intense than *a*, *c* is not specially conspicuous, while *d* can be seen only with difficulty; *e* is much more intense than *f*; *h* can no longer be distinguished, appearing now only as a slight shading on the violet edge of *g*; *j* is becoming very faint and hazy. The blue bands at λ 4475, 4427, and 4382 have changed very little in intensity, but have broadened somewhat.

At 600°, *a* is rapidly losing its identity, while *b* is still fairly distinct; *c*, *d*, *e*, and *f* have run into one band with an intensity maximum corresponding with the position of *e*. The band due to *g* and *h* has become very hazy and faint, while *j* can be seen only with difficulty. The three blue bands are still fairly distinct.

At the temperature which the oxide takes when held in the flame of the Bunsen burner the absorption agrees exactly with the emission as shown by the dotted curve in Fig. 2.

When rods of neodymium oxine are heated in the arc, or in the oxyhydrogen flame, the surface fuses as in the case of erbium oxide. The fused surface is, however, almost jet black, indicating that fused neodymium oxide is much less transparent than that of erbium. When sunlight is focused on the surface of this oxide, the bands may be seen, but they are so nearly drowned out by the admixture of white light reflected by the surface itself, that they are seen no better than when the fine powder is used. If the fused oxide could be made into very thin plates these would undoubtedly be transparent enough to allow the absorption spectrum to be seen with increased intensity, since by this method the reflected light would be very nearly eliminated.

It is stated in chemistries¹ that the oxide of neodymium (Nd_2O_3), if not heated too strongly, is pinkish in color, while if heated to a bright red it turns to a bluish-gray color. Some of the pink oxide was examined and was found to give an absorption spectrum which is quite different from that given by the gray oxide. Fig. 7 shows the two spectra compared. By heating the pink oxide to a bright red it changes into the gray variety. An attempt was made to prepare this pink oxide from the oxalate by heating it very gradually in an electric furnace; but nothing could be obtained except the gray oxide. Similar results were obtained when starting with the chloride, nitrate, or sulphate; at more or less elevated temperatures they change into the gray oxide, and at no stage could even a trace of the bands of the pink oxide be found. It would be interesting to know whether the pink oxide really has the same formula (Nd_2O_3) as the other variety, and if so, what the molecular differences are which cause such a marked change in the absorption.

c) Other compounds. The spectra of a number of compounds of both neodymium and erbium were observed both visually and photographically. These compounds were the chloride, oxychlorides, nitrate, subnitrates, sulphate, oxalate, and acetate of neodymium, and the nitrate, oxalate, and sulphate of erbium.

Fig. 8 shows the spectra of the chloride, nitrate, sulphate, and oxalate of neodymium, the salts being all dry. These illustrate quite well the fact that the absorption is different for the different compounds. There is, however, a general resemblance among the spectra shown in Fig. 8 (Plate IX). The group of bands in the yellow, for example, although different in structure in the different compounds, still occupies about the same position, and if viewed in a spectroscop of low dispersion might easily be thought to be the same in the four compounds. The same holds for the double group in the green.

Even this general resemblance disappears in some of the other compounds. If the chloride is heated in air it first changes into an oxychloride, and this finally into the gray oxide. The spectra of these three are shown in Fig. 9. It will be seen that the group of bands in the yellow seems to move toward the red as we pass from the chloride to the oxychloride to the oxide. Similar changes may

¹ O. Dammer, *Handbuch der anorganischen Chemie*, Vol. IV, p. 648.

be noticed for some of the other groups. Such changes are also noticed when the nitrate is heated so as to change into the subnitrate, and these into the gray oxide. This apparent "motion" of a "group of bands" may perhaps be what Becquerel refers to in the quotation cited above. On closer examination, however, it becomes evident that we are not dealing with the motion of a group as a whole, for the arrangement of the bands in the displaced group is very different from those in the original.

It may be a little difficult to say just what is meant by saying that a group of bands moves as a whole. Motion implies a continuous change of position, such as we have, for example, in the temperature change in the absorption bands of erbium oxide. Here we have nothing of that kind, for what actually takes place is this: the molecules of $NdCl_3$, for example, are capable of absorbing certain wave-lengths, which may, to be sure, vary slightly with temperature; similarly, the molecules of the neodymium oxychloride which is formed when the chloride is heated in air, are capable of absorbing certain wave-lengths, which will in general be different from those absorbed by the chloride. If the spectrum is observed while the chemical change is taking place, both sets of bands are found to be present, those belonging to the chloride gradually decreasing in intensity, while those belonging to the oxychloride increase until, when the chemical change is complete, the chloride bands have entirely disappeared. Unless a group of bands in the oxychloride corresponds band for band with a similar group in the chloride spectrum, we cannot very well say that we are dealing with the same group, for it is probable that the individual bands in the two cases are due to different vibrators.

The narrow band near $\lambda 4270$ shown by aqueous solutions of neodymium salts is interesting in this connection. It appears in very nearly the same position in solutions of the sulphate, chloride, acetate, and nitrate. In the nitrate it is, however, double, and in the solution of the acetate it is wider than in solutions of the chloride or sulphate. In the dry salts a narrow band appears in about the same region, the wave-length being in general somewhat greater. In the oxalate, for example, there is a band at $\lambda 4300$; in the chloride there is also a strong band at about $\lambda 4300$, but there are besides three fainter bands near it, which are equally narrow, one of which falls at

about λ 4280. In the oxychloride referred to already there is no band near λ 4300, but there are four very narrow bands beginning at about λ 4370, and extending toward λ 4425. The pink oxide has a band at about λ 4310, while the gray oxide has no band before we get to the red side of λ 4375. In view of these facts we cannot be sure that the band λ 4270 seen in solutions is found shifted toward the red in all dry compounds, for we may be dealing with entirely different bands.

d) Crystals. As stated above, Becquerel found that the absorption spectrum of a crystal depends somewhat upon the direction in which the (polarized) light is passed through it. This was also observed in the case of neodymium nitrate crystals in this work. Light was passed first through a nicol and then through a flat plate of $Nd(NO_3)_3$ about 2 mm in thickness. In a given position of the nicol some bands were seen which entirely disappeared if the nicol was turned through 90° . The reason for this is of course that the crystals are doubly refracting and the absorption is different in the two rays. This was seen in a very striking manner in a small crystal of erbium chloride. The crystal was in the form of a small prism having a refracting angle of about 30° . When light was passed through this prism, the ordinary and extraordinary rays were separated very nearly as widely as they are in an Iceland spar prism of the same angle. The absorption in the two rays was seen to be quite different. Unfortunately the crystal melted before a determination of its optic axis could be made, but polariscopic observations on both chloride and nitrate of erbium and neodymium indicate that the double refraction of these substances is at least twice as great as in Iceland spar.

If the spectrum of a crystal is compared with that of the corresponding dry salt, we still find some differences, but they are very slight compared to those mentioned above. Fig. 10 shows the change in the absorption of erbium sulphate crystals when these are heated more and more: that is, when the water of crystallization is driven off. (The sulphates of both neodymium and erbium part with their water of crystallization without decomposition, by simply being heated in the open air.) The change illustrated in Fig. 10 is very similar to that due to temperature in the case of erbium oxide. The bands due to the crystals are wider than those of the dry salt, and are also

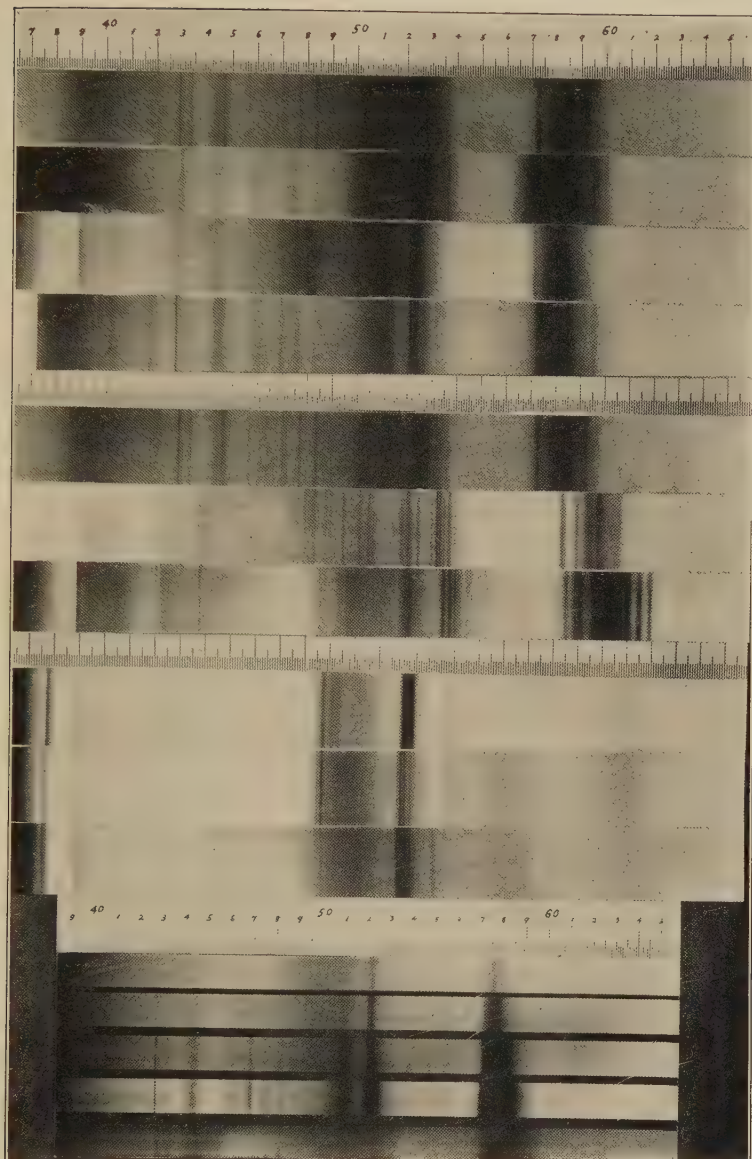
PLATE IX

FIG 8

FIG. 9.

FIG 10.

FIG II.



somewhat displaced toward the red. The displacement toward the red is also shown by neodymium sulphate, but the difference in width and general appearance of the bands is not very marked.

4. *Absorption of solutions.*—So much work has already been done on the absorption spectra of solutions of neodymium and erbium, that little attention was given to them in this work; it seemed, however, of some importance to compare the spectrum of a solution directly with that of the crystals obtained from it; and accordingly the spectra of solutions of the chloride, nitrate, sulphate, and acetate in various concentrations and those of the corresponding crystals were photographed to the same scale so that comparisons could be made with ease. Fig. 11 shows the absorption of an aqueous solution of the sulphate of neodymium in concentrations varying from $\frac{1}{8}$ normal to $\frac{1}{64}$ normal, compared with the absorption of the crystals deposited from the stock solution of sulphate. The general resemblance between the spectra is very apparent, but there are, however, differences especially well marked in the group in the yellow. In the crystals this group is seen broken up into individual bands, while in the more concentrated solutions, although the width of the group is smaller, the bands are not separated. In the $\frac{1}{32}$ normal solution the yellow group is seen broken up into four or five bands, whose positions are, however, different from the bands seen in the spectrum of the crystal. A $\frac{1}{16}$ normal solution of either the chloride or the nitrate shows the group broken up exactly as it is in the sulphate solution, although, as we have seen above, the bands in this group, in case of the crystals of the nitrate and chloride, are quite different.

Speaking very generally, it may be said that the spectra of solutions of different salts are nearly alike, while the spectra of the dry salts are very different. The spectra of the crystals seem to be, as it were, intermediate, differing from the two extremes much less than the extremes differ from each other.

DISCUSSION OF RESULTS

It has been shown that the absorption of the solid oxide at high temperatures corresponds exactly to the emission at the same temperature in accordance with Kirchhoff's law. This shows that the emission and absorption of the oxides, and presumably also of the

phosphates, are really both due to the same vibrators. The absorption of the oxide is very similar to that of other solid compounds, so that it is reasonable to suppose that the mechanism of the absorption spectrum of all solid compounds is the same. The general resemblance between the spectrum of a dry salt, the crystals, and the corresponding aqueous solution indicates that these are also due to the same thing. It seems reasonable therefore to assume that the three kinds of spectra defined above are due to the same vibrators, and there remains only to find the causes which produce the variations which are observed.

Let us assume that the vibrators in question are electrons located inside the metallic atom; these electrons are held in positions of equilibrium by forces due partly to the positive charge of the atom itself and partly to the other electrons inside it. It is evident that an atom consisting of a region positively charged and having in it a number of electrons whose combined charge is sufficient to neutralize the positive charge, although neutral for a point far away from its center, will still exert forces on charged bodies near it; or, we may say, the electric field of a Saturnian atom vanishes for points far removed from the atom, but not for points in its immediate neighborhood. It is also evident that the field in the immediate neighborhood will be different for atoms of different substances.

Now, to fix ideas, let us consider a neodymium atom having inside it certain electrons which may be set in vibration by light-waves falling upon them. If an atom of another substance such as chlorine is brought very near to it, the electric field of the chlorine atom will affect the periods of these electrons. It is also to be expected that an oxygen atom will produce a different change in the period, since its electric field is undoubtedly different from that of the chlorine atom. This indicates why the different compounds should show different absorption spectra.

To explain the temperature change, which, as we have seen, consists chiefly of a widening of the bands, we have only to consider that the periods of the vibrators will be a function of the distance between the disturbing atom and the atom containing the electron. If this distance is continually varying, that is, if the two atoms are vibrating with reference to each other, the period of the electron will also be

changing; in other words, the absorption it occasions will be a band rather than a line. Now, with increasing temperature the oscillations of the atoms in a molecule have their amplitudes increased and hence we should expect the bands to widen.

That the presence of water of crystallization should produce a change similar to that of raising the temperature indicates that the presence of water molecules diminishes the forces holding together the atoms forming the molecule, thus increasing the amplitudes of the oscillations; this is also what might be expected when it is considered that water has great dissociating powers, which depend primarily upon diminishing the forces holding the parts of a molecule together.

The fact that the spectra of aqueous solutions of different salts of the same element are so nearly alike may be due partly to the fact that the salts are dissociated, and hence the metallic ion is surrounded by water molecules, and hence would be in almost the same condition, no matter what salt is dissolved. It is also probable that even if the molecule of the dissolved salt is not dissociated, the effect of the molecules of the solvent in modifying the periods of the vibrating electrons would be very great.

SUMMARY

The results may be summed up in the following statements:

1. The bright band emission spectra of the oxides of erbium and neodymium are due to the oxides themselves, and correspond exactly to their absorption at the same temperature.
2. The absorption of the solid compounds changes with temperature, the change consisting in a widening of the bands, and in some cases a shift toward the red, as the temperature is increased.
3. The absorption spectra of dry compounds are different for different compounds of the same element.
4. The presence of water of crystallization in a compound seems to change its absorption in the same way that a rise in temperature does.
5. The results are satisfactorily accounted for by assuming that the vibrator responsible for the spectra is the electron inside the metal-

lic atom, its period of vibration being affected by the presence of other atoms or molecules.

In conclusion I wish to thank Professor Ames, who suggested the work, and under whose direction it was carried out, for his unfailing interest and many valuable suggestions.

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